

The Applicant has amended claim 47 to include two additional limitations: 1) that the second layer be sufficiently rigid to transmit stresses to the third layer; and 2) that the third layer have sufficient tensile strength to support a portion of the stresses experienced by the conduit.

New claim 61 and the amendments to claim 47 are supported by the specification as originally filed at page 22, line 15 to page 23, line 27; page 24, lines 1-12; and page 26, line 2 to page 27, line 8.

The Examiner has rejected claims 47-49, 52 and 53 as being unpatentable over Bertram et al., U.S. Pat. No. 4,792,493 (the '493 Patent) in view of Ranney et al., U.S. Pat. No. 4,015,044 (the '044 Patent).

The Examiner states that the '493 Patent, which issued to the Applicant, teaches the treatment of concrete or metal surfaces to yield surfaces having polyurethane intermediate layers and PVC inner layers bonded thereto. The Examiner further states that the PVC layer of the '493 Patent may be prepared by flame or corona treatment and by coating it with a polyurethane primer-activator, which suggests its impregnation with a bonding agent.

Although the '493 Patent discusses surface treatment of the thermoplastic sheet, the Applicant submits that the '493

Patent does not suggest impregnation thereof (see '493 Patent col. 4, lines 32-50).

Both the '493 patent and the present application discuss surface treatment of the thermoplastic sheet. However, two different conditions are obtained from these methods.

The surface treatment of the '493 patent involves roughening with a flame or corona discharge or by application of methylacetylene propane, (see '493 Patent col. 4, lines 32-50) which creates a micro-profile on the thermoplastic sheet, thereby enabling the thermosetting material to mechanically bond to the thermoplastic sheet. A clear moisture-cured polyurethane primer-activator is then applied to the thermoplastic sheet. The clear moisture-cured polyurethane primer-activator described in the '493 patent forms a covalent bond with the urethane thermosetting material but not with the thermoplastic sheet itself. The bond between the thermoplastic sheet and the clear moisture-cured polyurethane primer-activator is an adhesive bond (i.e., weak forces such as hydrogen bonds, Van der Waals forces, polar-polar bonds, etc.).

The thermoplastic sheet of the present invention can also be treated by ionizing or roughening the surface (see page 17, lines 8-14 of the present application). However, the surface treatment of the present application additionally involves the impregnation of the thermoplastic sheet with a hydroxyl-bearing resin having reactive sites that can form

covalent bonds with the urethane thermosetting material (see page 14, line 13 to page 15 line 13 of the present application). The bond between the hydroxyl-bearing resin and the thermoplastic sheet does not occur only at the surface of the sheet. Rather, the hydroxyl-bearing resin from the current application penetrates deep into the thermoplastic sheet by means of a solvent solution that swells the thermoplastic sheet. The highly branched, high molecular weight molecules of the hydroxyl-bearing resin are trapped in the matrix of the thermoplastic sheet as the solvent solution evaporates. In addition, compatibility and chemical bonding that occurs between the hydroxyl-bearing resin and the thermoplastic sheet keeps the hydroxyl-bearing resin from diffusing out of the matrix of the thermoplastic sheet. The free hydroxyl groups impregnated inside the thermoplastic sheet are available to react with the free isocyanato groups from the urethane thermosetting material, which diffuses into the internal structure of the thermoplastic sheet. This results in an interphase region between the thermosetting material and the thermoplastic sheet, which is characterized by covalent bonds between the impregnated thermoplastic sheet and the urethane thermosetting material. In contrast, the interface between the thermoplastic sheet and thermoset of the '493 Patent consists of simple surface adhesive bonds.

The thermoplastic sheet of the '493 patent is prepared for bonding with the urethane by applying a clear moisture-cured polyurethane primer-activator containing aromatic

solvents (see '493 Patent col. 4, lines 42-45). However, this is not the same as impregnation of the thermoplastic sheet of the present application with a reactive resin (i.e. hydroxyl-bearing resin). The clear moisture-cured polyurethane primer-activator containing aromatic solvents from the '493 patent does not penetrate and impregnate the thermoplastic sheet. It is, rather, a surface adhesive treatment that has free isocyanato reactive groups available to react and cross-link with hydroxyl groups in the urethane thermosetting material. In addition to the differences discussed above, there are a couple of disadvantages when comparing this method to that of the present invention. Firstly, the reliability of the bond between the activated thermoplastic sheet and the urethane thermosetting material of the '493 Patent is affected by ambient moisture content and by application timing. Secondly, and most importantly, the bond strength between the moisture-cured polyurethane primer-activator and the thermoplastic sheet of the '493 Patent is not sufficient for structural composite sandwich construction application. This is due to the fact that the bond is produced at the surface of the thermoplastic sheet, and no penetration or impregnation of the sheet takes place.

The hydroxyl-bearing resin of the present invention penetrates deep into the thermoplastic sheet forming a strong internal bond with it. The free hydroxyl groups impregnated inside the thermoplastic sheet are available to react with the free isocyanato groups from the urethane

thermosetting material, which diffuses into the internal structure of the thermoplastic sheet. The hydroxyl groups impregnated in the thermoplastic sheet are not susceptible to reaction with ambient moisture, so ambient moisture content and application timing do not affect the quality of the bond. Therefore, the present invention provides a more reliable, stronger bond between the thermoplastic sheet and the thermosetting material.

The urethane thermosetting material of the '493 Patent contains an isocyanate-bearing curing agent as does the thermosetting material of the present invention, and as do all polyurethanes. However, the urethane thermosetting material of the '493 Patent does not contain an excess concentration of isocyanato groups with respect to the concentration of hydroxyl groups in the thermosetting material and at the surface of the thermoplastic sheet. In contrast, in the present invention it is imperative that the thermosetting material have an excess of isocyanato groups so that these can react with the hydroxyl groups that have been impregnated in the thermoplastic sheet. Referring to page 14, line 25 to page 15, line 2 of the present application, it is stated that;

"When the curing agent is mixed with the thermosetting resin in the gun 68, an adequate quantity of the isocyanate is calculated and included when conveying the mixture 54 in the delivery tube 62, for bonding with the hydroxyl ions resulting from the treatment of the surface 70 of the

polyvinyl chloride sheet 28. Where the thermosetting resin is polyurethane resin or substantially polyurethane resin, and the curing agent is substantially isocyanates, it has been found that a volumetric ratio of isocyanate to resin of from 1.02:1 to 1.10:1 will provide the necessary quantity of isocyanate."

The ratio of 1.02-1.10:1 indicates that an excess of isocyanate is required. It is desirable for the thermosetting material to have an excess of isocyanato groups so that the isocyanato groups can react not only with the hydroxyl groups at the surface of the thermoplastic sheet but also with the hydroxyl groups that have been impregnated in the thermoplastic sheet. In addition to providing increased bond strength between the layers of thermoplastic sheet and the thermosetting material, the excess of isocyanate provides an additional advantage over the '493 Patent. Because the isocyanato groups are not stable and can cure in the atmosphere prior to application, the bond between the thermoplastic and thermoset layers of the '493 Patent may be impaired thus defeating the bond.

In the above passage (more specifically, in the sentence at page 14, line 29 to page 15, line 2 of the present application) the ratio is expressed in terms of isocyanate to resin. However, the Applicant submits that it would be clear to anyone skilled in the art that it is in fact more accurate to express the ratio in terms of isocyanato groups

and hydroxyl groups. Accordingly, the Applicant has amended the passage so that the ratio is expressed in terms of equivalents of isocyanato groups and equivalents of hydroxyl groups. For example, a 1.02:1 equivalent ratio of isocyanate to hydroxyl groups means that 102 equivalents of isocyanato radicals in the curing agent are mixed with 100 equivalents of hydroxyl radicals in the resin material. That implies that there is an excess of 2 equivalents (or 2%) of isocyanato groups in the thermoset. The excess isocyanato groups in the thermoset are free to react with the hydroxyl groups that had been impregnated in the thermoplastic PVC sheet, resulting in the formation of a covalent bond between the thermoset and the thermoplastic sheet. The Applicant submits that the weight and volumetric ratios can be found from the equivalent ratio as follows:

$$\text{Equivalent ratio} \times (\text{Equivalent Weight of NCO Groups in Curing Agent}) / (\text{Equivalent weight of OH Groups in Resin}) = \text{Weight Ratio}$$
$$\text{Weight Ratio} \times (\text{Density of Resin}) / (\text{Density of Curing Agent}) = \text{Volumetric Ratio}$$

In addition to the differences discussed above, there are important qualitative differences between the '493 Patent and the present invention. In the '493 patent, the thermosetting material is an elastomer, not suitable for structural composite sandwich construction. In other

words, the '493 patent is only appropriate where the fundamental integrity of the conduit wall is substantially unimpaired (see for example, U.S. Pat. No. 5,389,692 at col. 3, lines 21-40 and U.S. Pat. No. 5,268,392 at col. 3, lines 7-23). In contrast, the thermosetting material of the present invention is a rigid, high strength material capable of withstanding structural loads with very little deflection.

The invention taught in the '493 Patent is meant to be used for corrosion protection only, and not for structural repair. Only a thin membrane of material is needed for this purpose, (see the '493 Patent col. 3, lines 45-51, and claim 5) and it has to be capable of spanning cracks in concrete to prevent inflow of ground water and leakage of hazardous materials from structure. The preferred embodiment of the invention of the '493 Patent is a system where the thermosetting material is an elastomeric rubber, with low modulus, low strength, and high flexibility (e.g., a joint sealant type material) to accommodate concrete thermal expansion and contraction, and concrete movement such as in an earthquake. In addition, the thermoplastic sheet has to be a thin flexible material to accommodate bends, odd shapes, and irregularities on the surface to be lined. Neither the thermosetting material nor the thermoplastic liner taught in the '493 Patent are suitable for structural composite sandwich construction.

In the present invention, high modulus and high strength are stressed as characteristics necessary for producing a structural composite, very similar to those used in the aerospace industry. The system of the present invention, and each of its components, were developed to both protect concrete from corrosion, and to provide significant structural improvement over traditional steel reinforcement of concrete structures. Laboratory testing has verified that these materials provide improved reinforcement when compared to steel, by distributing loads and preventing stress concentrations.

Applicant reiterates that none of the references cited by the Examiner, alone or in combination, discloses means for strengthening a pipe or conduit. More specifically, there is no suggestion that the invention of the '493 Patent contributes to the tensile, compressive, or flexural strength of the host structure. In fact, the elastomeric nature of the thermosetting layer of the '493 Patent and the relatively thin aspect of the thermoplastic and thermosetting layers make it impossible for the invention of the '493 Patent to contribute appreciably to the structural strength of the conduit. The Applicant further submits that it is well known in the art that the invention of the '493 Patent cannot be used to repair pipes or culverts that have lost part of their steel reinforcement due to corrosion, and thus have lost their load bearing capacity.

In the composite structure of the present invention the stresses experienced by the structure due to externally and internally applied loads (e.g., earth loads, live loads, hydrostatic pressure from ground water, etc.) are transmitted and transferred to the PVC via the thermosetting material. When stresses are transferred from the corroded host structure to the PVC liner, the host structure is effectively reinforced and the load bearing capacity of the original structure is improved. The amount of stress transferred from the host structure to the PVC liner depends mainly on the material properties of the PVC liner and thermosetting material, and on the thickness of each of these sections. The most relevant material properties are: (1) The modulus of rigidity and strength of the PVC liner, (2) the shear modulus of rigidity, and shear strength of the thermosetting material, and (3) the normal and shear bond strengths between the thermosetting material and the host structure, and between the thermosetting material and the PVC liner. The treated PVC liner of the present invention is chemically bonded to the thermosetting material by means of strong covalent bonds extending into the thermoplastic sheet, whereas the bond between the thermoplastic sheet and thermoset of the '493 Patent is an adhesive bond. The continuous covalent bonding of the present invention provides superior transfer of stresses from the host structure to the PVC liner, resulting in a significantly reinforced and strengthened structure.

In particular, the flexural stiffness and strength of the host structure are improved when the method described by the Applicant is applied on faces of the host structure that are under tension as a result of an applied bending moment. This circumstance occurs at the crown of all buried pipes and culverts. In turn, the crown is the part of a concrete pipe or culvert that is most susceptible to hydrogen sulfide induced corrosion, and it is the part that most frequently requires structural repair. Under the above-mentioned circumstances, the PVC sheet, via the thermosetting material, behaves as tensile steel reinforcement.

The Applicant has proven via testing that the application of the present invention can increase the strength of a corroded host pipe with severe structural damage (i.e., missing steel reinforcement) by 300 to 400 percent over the original design strength of the uncorroded pipe.

In summary, the Applicant submits that the '493 Patent does not disclose impregnation of the thermoplastic sheet with a hydroxyl-bearing resin having reactive sites that can form covalent bonds with the urethane thermosetting material. The strength of the covalent bonds between the hydroxyl-bearing resin and the thermosetting material allows for the transfer of stresses between the thermoset and the thermoplastic sheet. The Applicant submits that none of the references cited by the Examiner discloses means for strengthening a deteriorated pipe or conduit. In addition,

the elastomeric nature of the thermosetting material of the '493 Patent, and the thinness of the thermoplastic and thermosetting layers indicate that the invention of the '493 Patent has an insufficient modulus of rigidity and strength of the PVC liner and insufficient shear modulus of rigidity, and shear strength, of the thermosetting material to appreciably improve the structural strength of the conduit.

In view of the foregoing amendments and remarks, favorable reconsideration of the Application is respectfully solicited.

Respectfully submitted,

Dated: 10/16/02

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with the blowing agent from the hose 60 at the gun 68, which is a substantial distance from the nozzle 64, the resin, curing agent and gas should expand substantially by the time the cellular material 54 is shot from the nozzle 64. There is some weight in the cellular material 54, and the thermoplastic sheet 28 must be rigid enough to support this weight when the cellular material 54 has filled the space 36. It has been found that for a conduit 14 of approximately sixty inches or five feet original interior diameter, and where the cellular material 54 is a polyurethane foam having a density of from approximately 17 pounds per cubic foot to 23 pounds per cubic foot, a polyvinyl chloride sheet having a flexural modulus of approximately 500,000 plus or minus 150,000 is suitable. It is believed that the polyurethane foam will perform best and provide the necessary restoration in densities ranging from ten pounds per cubic foot to fifty-five pounds per cubic foot.

The thermoplastic material of sheet 28 is in the preferred embodiment a polyvinyl chloride. The sheet has two faces. A first face 70 faces the space 36 and interior surface 22 of the substrate 18. The second face 71 faces the interior of the substrate 18. The face 70 facing the space 36 is treated prior to installation within the conduit 14, by treating that surface with 2-propenoic acid, 2-hydroxypropyl ester, polymer with chloroethene and ethenyl acetate reactive resin having a density of 1.37 grams per cubic centimeter at 25 degrees Centigrade and a molecular weight of from 8,000 to 10,000. The reactive resin may contain a catalyst to enhance and cause a preference for a molecular linkage between the thermoplastic sheet 28 and the thermoset material 54. Such a treatment impregnates the polyvinyl chloride sheet 28 through that surface 70, leaving hydroxyl ions along with the catalyst on the surface 70 available for bonding with the isocyanate or other bonding agent which is part of the curing agent for the thermosetting resin. When the curing agent is mixed with the thermosetting resin in the gun 68, an adequate quantity of the isocyanate is calculated and included when conveying the mixture 54 in the delivery tube 62, for bonding with the hydroxyl ions resulting from the treatment of the surface 70 of the polyvinyl chloride sheet 28. Where the thermosetting resin is polyurethane resin or substantially polyurethane resin, and the curing agent is substantially isocyanates, it has been found that a volumetric ratio of

isocyanate to resin of from 1.02:1 to 1.10:1 of equivalents of isocyanato groups to equivalents of hydroxyl groups will provide the necessary quantity of the isocyanate.

When the thermoset 54 is filled within the space 36, the isocyanate will chemically bond with the available hydroxyl ions embedded to the sheet 28 to create an integrated, composite structure comprising a polyvinyl chloride region at one end, a region on the other end comprising the cellular thermoset material 54, and, in progressing across the cross-section from one to the other, an interphase region 74 where the polyvinyl chloride with its available hydroxyl ions have molecularly integrated with the isocyanate of the cellular thermoset 54. This bonding is universal and generally complete over the entire active treated area of the first face 70 of the polyvinyl chloride sheet 28, and the corresponding area of the thermosetting material 54 coming into contact with the face 70 after the thermosetting material cures and sets.

The thermosetting resin preferably comprises a polyurethane resin. The resin has mixed in it suitable surfactants, amines and silanes. The characteristic of silane allows the material of which it has been included, to bond chemically with many minerals commonly present in most cementitious, ceramic and metallic substrates, of which most sewer conduits are made. Suitable silanes can be obtained commercially. Silanes will chemically bond with the substrate 18, whether made primarily of concrete or other cementitious material, or clay, brick or metal.

The insertion of the expanded, cellular thermosetting material 54 into the space 36 allows the thermosetting material 54 to work into the pores and interstices 76 of the substrate 18. A suitable surfactant or surfactants may be added to the thermosetting material 54 in order to facilitate such working of the thermosetting material 54 in order to facilitate such working of the thermosetting material 54 into these pores and interstices 76 emanating into the substrate 18 from the corroded surface 22, as more fully described in my patent No. 5,389,692, the description of which is incorporated herein as though fully set forth in detail. The silane in the thermosetting material 54 will chemically bond to the substrate 18, to establish an interphase region 75 between what ultimately becomes the thermoset 54 and the substrate 18. The thermoset material 54 and the substrate 18

I CLAIM:

47. A corrosion-resistant chemically continuous composite conduit having an inside and an outside, said conduit comprising from the outside to the inside:

- a) a first layer comprising a porous, mineral-containing substrate;
- b) a second layer comprising a thermosetting material, said thermosetting material containing a silane and a curing agent comprising isocyanate groups;
- c) a third layer comprising a thermoplastic material, said thermoplastic material impregnated with a reactive resin;

wherein an interface between said first and second layers comprises covalent bonds between said silane in said second layer and minerals in said first layer;

wherein an interface between said second and third layers comprises covalent bonds between said isocyanate groups of said second layer and said reactive resin of said third layer;

wherein said second layer is sufficiently rigid to transmit stresses between said first and third layers;

wherein said third layer has a tensile strength sufficient to support a portion of said stresses; and

wherein said first, second and third layers are bonded together with sufficient shear strength to transmit and distribute said stresses ~~loads~~ between said layers.

48. The conduit of claim 47, wherein said first layer comprises a cementitious, ceramic, clay, brick, or metallic substrate.

49. The conduit of claim 47, wherein said thermosetting material is polyurethane resin.

50. The conduit of claim 47, wherein said thermosetting material contains a surfactant.

51. The conduit of claim 47, wherein said reactive resin is 2-propenoic acid, 2-hydroxypropyl ester, polymer with chloroethene and ethenyl acetate.
52. The conduit of claim 47, wherein said thermoplastic material is PVC.
53. The conduit of claim 47, wherein said PVC has a tensile strength of ~~between~~ 5,000 to 10,000 psi.
54. A method for lining a porous, mineral-containing conduit, said method comprising the steps of:
- a) impregnating a sheet of thermoplastic material with a reactive resin;
 - b) positioning said sheet of thermoplastic material within the interior of said conduit spaced apart from an inner surface of said conduit;
 - c) inserting a thermosetting material between said sheet of thermoplastic material and said inner surface, said thermosetting material containing a silane and a curing agent comprising isocyanate groups;
- wherein said silane forms covalent bonds with said minerals in said conduit;
- wherein said isocyanate groups form covalent bonds with said reactive resin of said thermoplastic sheet,
- wherein said thermoplastic sheet, said thermosetting material, and said conduit are bonded together with sufficient shear strength to transmit and distribute loads between them.
55. The method of claim 54, wherein said conduit comprises a cementitious, ceramic, clay, brick, or metallic substrate.
56. The method of claim 54, wherein said thermosetting material is polyurethane resin.
57. The method of claim 54, wherein said thermosetting material contains a surfactant.

58. The method of claim 54, wherein said reactive resin is 2-propenoic acid, 2-hydroxypropyl ester, polymer with chloroethene and ethenyl acetate.
59. The method of claim 54, wherein said thermoplastic material is PVC.
60. The method of claim 54, wherein said PVC has a tensile strength of ~~between~~ 5,000 to 10,000 psi.
61. The conduit of claim 47, wherein said stresses include compressive, tensile and shear stresses due to one or more of earth loads, live loads and hydrostatic loads.